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Solubility of Anhydrous $AlCl_3$ in $TiCl_4$ and VCl_4

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	μm	micrometer
h	hour	psi	pound per square inch
K	kelvin	rpm	revolution per minute
L	liter	wt pct	weight percent
mL	milliliter		

SOLUBILITY OF ANHYDROUS $AlCl_3$ IN $TiCl_4$ AND VCl_4

By Dennis A. Hansen[1] and Davis E. Traut[2]

ABSTRACT

The solubility of anhydrous aluminum chloride in solutions of titanium tetrachloride and vanadium tetrachloride was determined as part of a research project by the Bureau of Mines to make a homogeneous alloy sponge of titanium, vanadium, and aluminum. Solubility curves were established using an autoclave at 75°, 100°, 125°, and 150° C. The solubility of $AlCl_3$ in $TiCl_4$ is 0.2 wt pct at 75° C; it increases to 18.3 wt pct at 150° C. The data concur with data from earlier researchers of this binary system for 75° to 125° C. For the VCl_4-$AlCl_3$ binary system the solubility of $AlCl_3$ is 0.1 wt pct at 75° C, increasing to 1.6 wt pct at 150° C. For the $TiCl_4$-$AlCl_3$-VCl_4 ternary system the solubility of $AlCl_3$ decreases from the values found with a pure $TiCl_4$-$AlCl_3$ system to the lower values found with a pure VCl_4-$AlCl_3$ system at the respective temperatures.

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INTRODUCTION

The Bureau of Mines is conducting studies on several approaches to make high-quality titanium alloy powder. Savings in cost and reduction of waste may be realized in the production of titanium alloy products by the use of powder metallurgy techniques to produce high quality, near-net-shape parts. Several methods for producing spherical, high-purity titanium alloy powder are being investigated throughout the industry, but only one method, the *P*lasma *R*otating *E*lectrode *P*rocess (PREP), has been proven to produce a powder of high enough quality for use in aircraft manufacture (1).[3] Production of powder by the PREP process is expensive because of the necessity of using electrodes accurately machined and ground from billets forged from double- or triple-arc-melted alloy ingots. Direct production of spherical alloy powder from titanium alloy sponge could eliminate most of these costly melting steps and result in significant cost savings.

In the approach used by the Bureau (2) to make alloy sponge, the chlorides of titanium (Ti), vanadium (V), and aluminum (Al) are simultaneously reduced by magnesium (Mg) via a Kroll-type reaction. A homogeneous (as to Ti, Al, and V distribution) powder is considered essential for final titanium alloy part integrity (3). (Thus, both a homogeneous titanium alloy sponge and a homogeneous metal chloride feed are required to make the powder.) At room temperature, titanium tetrachloride ($TiCl_4$) and vanadium tetrachloride (VCl_4) are liquids, while aluminum chloride ($AlCl_3$) is a solid. A dispersion of minute, solid $AlCl_3$ particles in the liquid $TiCl_4$-VCl_4 phase would not be desirable, as this would adversely impact homogeneity (2, p. 20). Therefore, the solubility relationship of $AlCl_3$ in a $TiCl_4$-VCl_4 solution was required to properly prepare feed solutions for the Kroll work, but this relationship was not found in the literature. The solubility data available were limited to the solubility of $AlCl_3$ in $TiCl_4$.

To determine the solubility of $AlCl_3$ in $TiCl_4$, Eingorn (4) used a thermal analysis method and investigated the system from -24° to 120° C. Through a lateral extension in a glass vessel, just enough $TiCl_4$ was poured in to cover the thermometer bulb. The melting temperature of the pure solvent was measured. Then a small amount of $AlCl_3$ was added and the temperature of crystallization was again determined to establish a cooling curve.

Morozov (5) used a saturation method from 18° to 80° C and a thermal analysis method from 93° to 193° C. In both methods a sealed vessel was used. For the saturation method the chlorides were sealed in one arm of a two-armed glass apparatus, and kept at the desired temperature for 20 to 40 h. Then part of the transparent supernatent was poured into the unused arm. This arm was then cut off and the solution analyzed. For the thermal analysis method a known weight of each of the chlorides was placed in a sealed apparatus, and the apparatus was subjected to heating and cooling. The resulting temperature was measured by a pyrometer. Morozov's results are currently used as a reference (6).

Druzhinina (7) used a saturation method from 55° to 150° C, very similar to that used by Morozov. As with Morozov, the clear supernatent was decanted from one test tube leg to another in a sealed system. Mixing was done periodically by shaking the test tube apparatus. From 4 to 6 h was required to reach equilibrium saturation. Druzhinina found that the thermal analysis method for determining solubility of this system was not satisfactory owing to the supersaturation of $AlCl_3$ in $TiCl_4$.

Ehrlich (8) used a saturation method from 25° to 125° C in which the chlorides were combined in a stirred container for an unspecified time to reach equilibrium. Then a sample was taken. Ehrlich commented that the data obtained by Morozov could not be confirmed and that the

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

solubility values of $AlCl_3$ in $TiCl_4$ determined by Morozov were about 10 times higher than his own solubility values.

Ruban (9) also used a saturation method from 70° to 127° C, but with an unsealed reaction vessel. The equilibrium time for each temperature was determined; it ranged from 38 to 40 h at 70° C down to 15 to 20 h at 127° C. Ruban expressed concern that the 6-h equilibrium time used by Druzhinina was too short and thus produced low $AlCl_3$ solubility.

Martynov (10) used a saturation method from -20° to 50° C in a stirred quartz vessel (11). Martynov compared the data of Ehrlich, Druzhinina, Ruban, and Morozov with his own and found the data of Morozov to be significantly different from data from all other investigators.

The emphasis of this study was the solubility of $AlCl_3$ in a $TiCl_4$-VCl_4 system. It was not the initial intent of this study to duplicate the previous studies on the $TiCl_4$-$AlCl_3$ system as they seemed adequately done. However, the materials in both systems are difficult to work with since they hydrolyze easily. Therefore, a careful review of previous researchers' methods and a duplication of their results in the $TiCl_4$-$AlCl_3$ system would confirm the Bureau's experimental method and procedures as applied to not only the $TiCl_4$-$AlCl_3$ system but also to the $TiCl_4$-$AlCl_3$-VCl_4 system.

Morozov was the only researcher who used the thermal analysis method to determine solubility (5). The data obtained in that study are not consistent with four other studies. Ruban suggested that the thermal analysis method may not allow the system to reach equilibrium saturation owing to insufficient time at a specific temperature. In addition, the method would require the determination of solution composition by the input of known weights and volumes of the materials rather than actual analysis. Both the possible hydrolysis of the materials used and the instability of VCl_4 might prevent the accurate determination of these weights and volumes. For these reasons the saturation method was chosen to determine the solubility relationship in the $TiCl_4$-$AlCl_3$, VCl_4-$AlCl_3$, and $TiCl_4$-$AlCl_3$-VCl_4 systems in this study.

MATERIALS

The spectrographic analyses of compounds used as starting materials are shown in table 1.

Anhydrous $AlCl_3$ was purified by subliming technical-grade $AlCl_3$ in a glass reactor inside an electric tube furnace that was held at a temperature above the sublimation temperature of 182.7° C (12). The sublimed $AlCl_3$ was swept away with argon carrier gas to another chamber, where it was condensed as a white powder using water-cooled coils.

The $TiCl_4$ was distilled in a 5-L round-bottomed flask containing 2 L of $TiCl_4$, and the condensed vapor collected in a 2-L flask. The system was purged with argon prior to use. The distillate was then redistilled using the same methods. The double-distilled $TiCl_4$ was colorless.

The VCl_4 was triple distilled by the same methods used for the $TiCl_4$. This VCl_4 distillate was dark brown. VCl_4 is known to be unstable and decomposes very slowly at room temperature into solid VCl_3 and Cl_2 gas. This decomposition is increased by temperature but hindered by pressure of the product Cl_2 gas, and usually must be photochemically or

TABLE 1. - Spectrographic impurity analysis,[1] weight percent

Ion	$AlCl_3$	$TiCl_4$	VCl_4
Al.....	>10	<0.01	ND
Cu.....	<.003	<.003	ND
Fe.....	<.01	<.01	<0.01
Mg.....	<.01	ND	ND
Ni.....	<.03	<.1	<.1
Si.....	<.01	<.01	<.01
Ti.....	<.03	>10	<.3
V.....	<.3	ND	>10
Zn.....	<.03	ND	ND

ND Not detected.

[1]The materials were also analyzed for the following elements, but none was detected: Ag, B, Be, Ca, Cb, Cd, Co, Cr, Hf, Mn, Mo, Na, P, Pb, Pt, Sb, Sn, Ta, W, Zr.

catalytically initiated (14-15). However, VCl_3 is insoluble in $TiCl_4$ (8) and in nonpolar solvents such as VCl_4 (16). The presence of VCl_3 in this study of the ternary system of $TiCl_4$-$AlCl_3$-VCl_4 and the binary VCl_4-$AlCl_3$ system was not desired but was not preventable nor measurable. However, this presence of insoluble VCl_3 and Cl_2 gas should not influence the solubility of $AlCl_3$ in the ternary or binary systems.

All of the above compounds hydrolyze when contacted with water. Exposure to air and the contained humidity will easily hydrolyze $TiCl_4$ and VCl_4. Care in handling was therefore exercised.

EQUIPMENT

The apparatus used to contain and mix the metal chlorides during the solubility study was a 300-mL, stirred, stainless steel autoclave, shown in figures 1 and 2. Figure 1 includes the support stand, stirring assembly, and the heater. Figure 2 shows the top half of the reactor.

The reactor material was 316 stainless steel with the main vessel having a Teflon[4] fluorocarbon polymer liner. A fritted stainless steel (10-μm pores) filter prevented solid $AlCl_3$ and any VCl_3 present from entering the sampling tube. The sampling line outside the reactor was preheated using heat tape to prevent the $AlCl_3$ from precipitating out of solution before reaching the sample bottle. A sampling valve was located on the sampling line just above the sampling port. The mixture was stirred at 100 rpm with an impeller turned by an adjustable-speed electric motor, drive belt, and pulley system. A series of packing cones and spacers around the shaft and inside the air-cooled packing gland kept all vapors inside the reactor. A safety rupture disc, rated at 2,000 psi, was used. A type J (iron-constantan) thermocouple inside the reactor was connected to a potentiometer, using an ice bath as a reference temperature. This thermocouple indicated the actual process temperature. Another type J thermocouple was located between the heating mantle and the reactor. This thermocouple was connected to the autoclave temperature controller and

[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

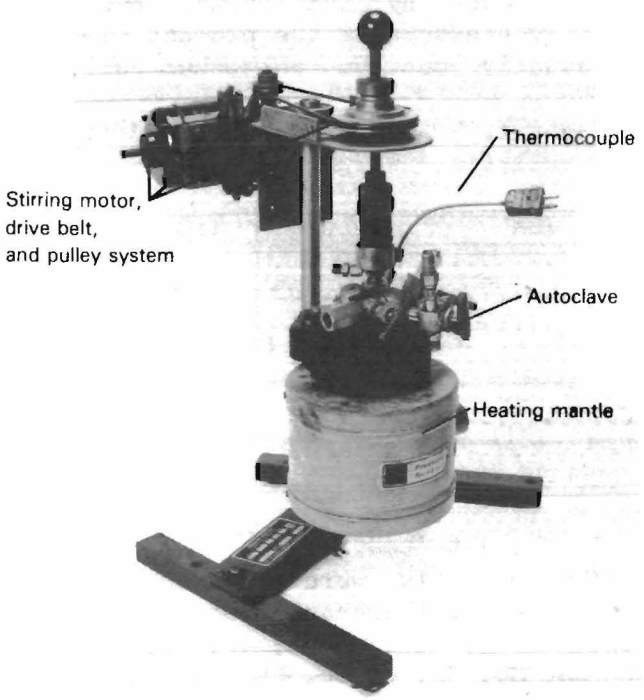

FIGURE 1. - Autoclave assembly.

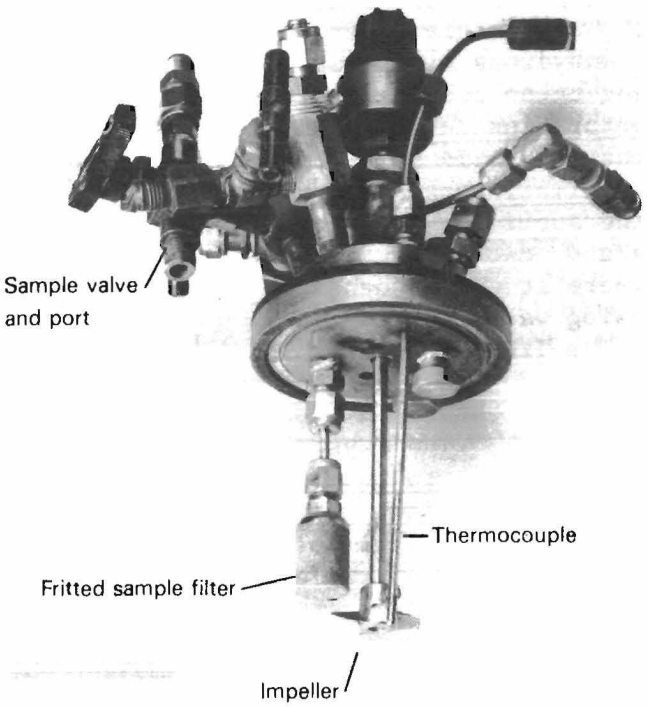

FIGURE 2. - Top half of autoclave.

was used to control the process temperature. A calibration curve relating the temperature inside the reactor to the temperature outside the reactor was used to set the controller temperature. This double thermocouple arrangement was recommended by the autoclave manufacturer to prevent wide temperature swings due to the thermal gradient of the Teflon liner. The apparatus was placed inside a glove box, which was filled with argon while the reactor was loaded and when the material was sampled. The glove box was vented to an exhaust hood.

EXPERIMENTAL PROCEDURE

An experiment was performed to determine the amount of contact time for the system to attain equilibrium. Ruban (9) had stated that at lower temperatures, greater time is necessary for equilibrium. For the present study, excess $AlCl_3$ was contacted with $TiCl_4$ at 75° C for times up to 144 h, and a sample was taken as soon as the system reached temperature and at various intervals after that time. A similar equilibrium study using VCl_4 at 75° C was also completed for times up to 144 h. No significant difference was found in the analysis of samples for times of 2 h or more. (See table 2.) Therefore, at least 2 h of contact time at the desired temperature was allowed before sampling during the solubility program.

Measurements of solubilities were made at 75°, 100°, 125°, and 150° C using the purified chlorides. The temperature was fixed but the pressure was not measured, as the effect of pressure on solubility is considered very small (16). For each run, an amount of VCl_4 in $TiCl_4$ was added to the vessel. This transfer was done in an argon atmosphere within a glove box. An excess amount of $AlCl_3$ powder was added to the vessel. The apparatus was assembled and the temperature controller was adjusted to an internal temperature of 75±0.5° C. The contents were left at each temperature for at least 2 h to reach equilibrium, as determined by the earlier study. Then under argon, approximately 5 mL of fluid was withdrawn and then discarded in order to purge the sample line. Two samples were then taken and quickly capped. The temperature controller was adjusted to the next higher temperature (100°, 125°, and 150° C) and the above procedure was repeated.

TABLE 2. - Equilibrium time for solubility of $AlCl_3$ in $TiCl_4$ and VCl_4 at 75° C

Contact time, h	$AlCl_3$, wt pct[1]	
	In $TiCl_4$	In VCl_4
0	0.21	0.08
0.5	ND	.08
1	.19	.08
2	.24	.09
4	.25	ND
24	.24	.09
48	ND	.08
72	.23	ND
96	.22	ND
120	.23	ND
144	.23	.08

ND Not determined.

[1]Values are the average of the samples taken at each time.

For analysis, each sample was added to a 1-L graduated cylinder containing 400 mL of ice and water. The sample bottle was rinsed three times with more ice water, and this rinse water was added to the graduated cylinder. After the ice melted, the mixture was stirred and about 25 mL of liquid was taken for analysis. About 5 mL of concentrated HCl was added to each sample to prevent precipitation of solids.

Titanium concentration was determined volumetrically using a solution of ferric ion as the titrant and thiocyanate ion as the endpoint indicator. Aluminum concentration was determined by atomic absorption spectrophotometry. Vanadium concentration was determined volumetrically using a solution of ferrous ion as the titrant and diphenylamine sulfonate as the endpoint indicator. Exact dilution and sampling quantities were not required, as only relative cations were analyzed. A calculation using these analyses for Ti, Al, and V was used to obtain the actual concentration of $TiCl_4$, $AlCl_3$, and VCl_4 in the original sample.

RESULTS AND DISCUSSION

The results are shown in figures 3-7, and summarized in table 3. The results for the $TiCl_4$-$AlCl_3$ binary system are shown in figure 3. Systems containing compositions that are above the solubility curve contain both solid $AlCl_3$ and saturated solution. Systems below the curve contain unsaturated solution. The curve represents systems that are saturated and contain no solid $AlCl_3$.

In figure 4, a comparison of existing data (4-5, 7-10) and the results obtained

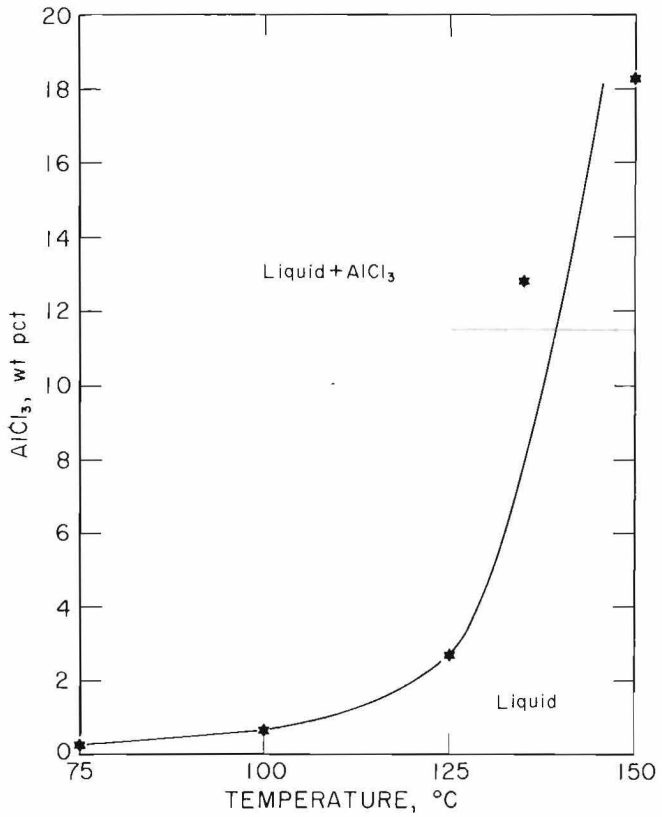

FIGURE 3. - Solubility of $AlCl_3$ in $TiCl_4$.

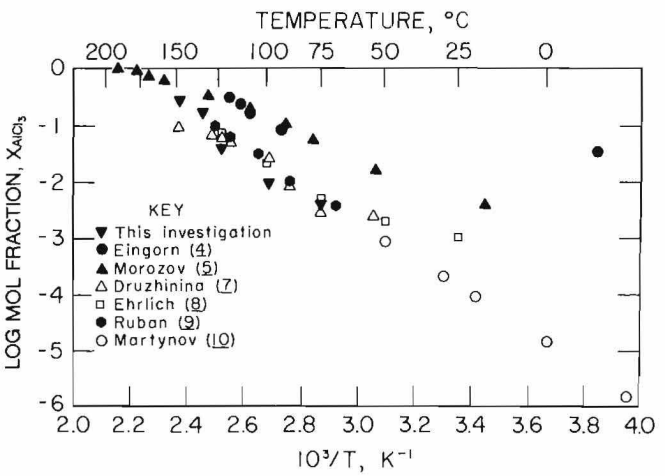

FIGURE 4. - Solubility of $AlCl_3$ in $TiCl_4$—a comparison of results.

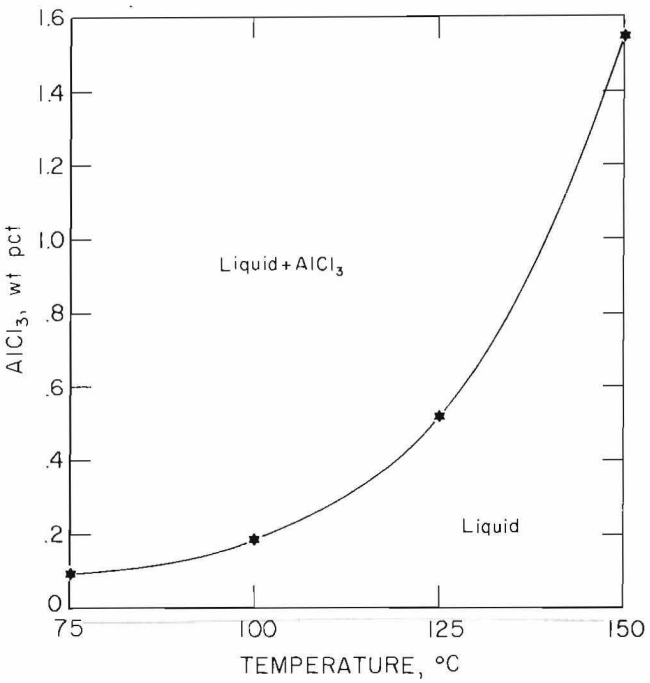

FIGURE 5. - Solubility of $AlCl_3$ in VCl_4.

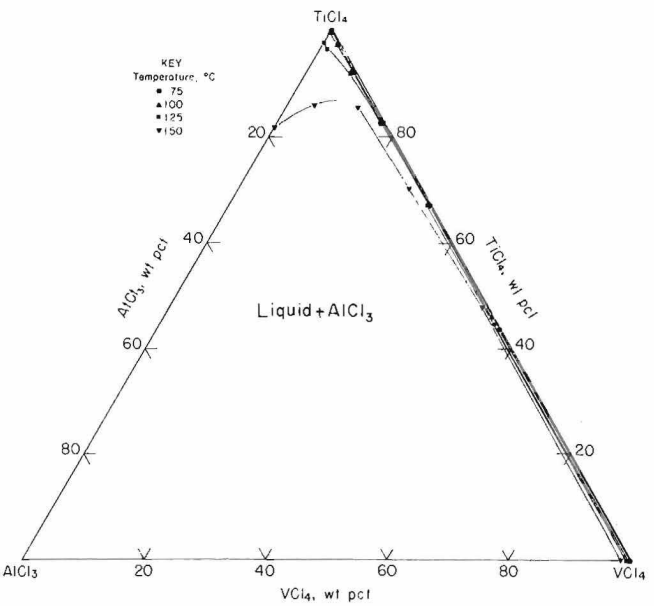

FIGURE 6. - Solubility of $AlCl_3$ in $TiCl_4$-VCl_4 system.

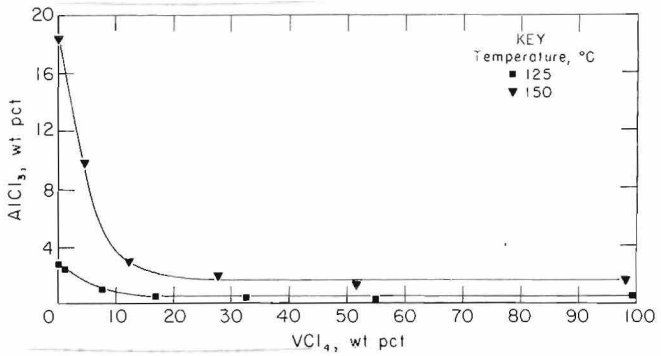

FIGURE 7. - Effect of VCl_4 concentration on $AlCl_3$ solubility in $TiCl_4$-VCl_4 system.

in this study for the $TiCl_4$-$AlCl_3$ binary system are shown. The log mol fraction versus $10^3/T$ plot shown as figure 4 has been used by other researchers to present their data and obtain thermodynamic values (9, 10). The data found in the present study were in good agreement with data of Druzhinina (7), Ehrlich (8), Ruban (9), and Martynov (10) for the 75° to 125° C region. However, at 150° C the solubility of $AlCl_3$ in $TiCl_4$ was 18.3 wt pct, compared with 7.2 wt pct as reported by Druzhinina and with 41.1 wt pct as interpolated from Morozov's data.

Figure 5 depicts results for the VCl_4-$AlCl_3$ binary system. The solubility of $AlCl_3$ in VCl_4 increased from 0.1 wt pct at 75° C to 1.6 wt pct at 150° C.

Figure 6 shows the solubility curves at 75°, 100°, 125°, and 150° C for the $TiCl_4$-$AlCl_3$-VCl_4 system. Generally, the solubility of $AlCl_3$ at 75° and 100° C is less than 1 wt pct for any mixture of $TiCl_4$ and VCl_4. At 150° C the solubility was found to be between 1 to 3 wt pct except when the VCl_4 is less than 12 wt pct.

Figure 7 shows the effect of VCl_4 concentration on the solubility of $AlCl_3$ in the $TiCl_4$-$AlCl_3$-VCl_4 system. The greatest solubility of $AlCl_3$ occurs in pure $TiCl_4$ (0 wt pct VCl_4) for each of the two temperatures shown. As any VCl_4 is introduced into the system, the solubility of $AlCl_3$ decreases. Temperature

TABLE 3. - Summary of solubility data[1] for the $TiCl_4$-$AlCl_3$-VCl_4 system,[2] weight percent

At 75° C			At 100° C			At 125° C			At 150° C		
$TiCl_4$	$AlCl_3$	VCl_4	$TiCl_4$	$AlCl_3$	VCl_4	$TiCl_4$	$AlCl_3$	VCl_4	$TiCl_4$	$AlCl_3$	VCl_4
99.76	0.24	-0-	99.36	0.64	-0-	97.18	2.82	-0-	80.75	19.25	-0-
99.76	.23	-0-*	99.33	.67	-0-*	97.16	2.84	-0-*	81.72	18.28	-0-*
99.77	.23	-0-	99.32	.68	-0-	97.88	2.12	-0-	82.52	17.48	-0-
99.77	.23	-0-	99.36	.64	-0-	96.83	3.17	-0-	82.65	17.35	-0-
97.17	.18	2.65	96.88	.61	2.52	96.63	2.07	1.30	88.47	11.53	0.21
97.28	.13	2.59*	96.93	.64	2.43*	96.57	2.18	1.26*	87.08	11.92	.18*
91.85	.14	8.01	93.58	.35	6.07	92.00	1.14	6.86	85.70	9.46	4.83
91.95	.16	7.89*	92.39	.30	7.31*	91.49	1.08	7.43*	85.77	9.78	4.45*
83.10	.17	16.73	83.01	.21	16.78	82.56	.47	16.97	83.62	3.24	13.15
82.57	.11	17.32*	82.71	.18	17.10*	82.78	.49	16.73*	84.96	2.87	12.18*
65.48	.08	33.75	67.43	.14	32.43	67.95	.42	31.64	67.72	2.35	29.93
66.72	.14	33.14*	67.20	.13	32.66*	66.86	.43	32.71	69.89	2.19	27.92*
43.46	.06	56.47	45.63	.08	54.28	47.51	.21	52.28	46.96	.99	52.05
43.40	.06	56.54*	46.04	.09	53.87*	44.86	.27	54.88*	47.32	1.27	51.41*
0	.11	99.89	0	.16	99.84	0	.60	99.40	0	1.62	98.38
0	.10	99.90*	0	.18	99.82	0	.52	99.48	0	1.55	98.45*

[1]In addition, 1 analysis at 135° C showed 87.10 wt pct $TiCl_4$, 12.90 wt pct $AlCl_3$, and 0 wt pct VCl_4.

[2]Values marked with an asterisk (*) correspond to values referred to in text that are usually the compositions of the 2d of 2 samples taken at a given time and temperature. It was felt in these cases that the 2d sample better represented the vessel's contents, as the 1st sample taken after the purge would have further purged the sample line and valve. However, very little difference was seen between the 2 sample analyses in any case.

increases the solubility of $AlCl_3$ in all combinations of solutions, but it has the greatest effect when less than 20 wt pct VCl_4 is present.

CONCLUSIONS

The solubility of anhydrous $AlCl_3$ in $TiCl_4$ and VCl_4 was studied by the Bureau of Mines as part of a research project to make a homogeneous alloy sponge of Ti, Al, and V. From this effort the following general conclusions may be drawn.

1. Data on the $TiCl_4$-$AlCl_3$ binary system are in good agreement with data of previous investigators for the range 75° to 125° C.

2. The $AlCl_3$ is more soluble in $TiCl_4$ than in VCl_4 at any of the temperatures studied.

3. In the $TiCl_4$-$AlCl_3$-VCl_4 ternary system, the solubility of $AlCl_3$ decreased from the values with a pure $TiCl_4$-$AlCl_3$ system to the lower values found with a pure VCl_4-$AlCl_3$ system at the respective temperatures.

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